Strained, ring tilted dicarbon-bridged [2]ferrocenophanes and ferrocene revisited: ^{57}Fe Mössbauer spectroscopic study of bonding, hyperfine interactions, and lattice dynamics

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Abstract

The temperature dependencies of the nuclear hyperfine interactions (isomer shift, quadrupole splitting and resonance effect magnitude) for two [2]ferrocenophanes have been studied by ^{57}Fe Mössbauer effect spectroscopy over the temperature range from 90 K to above room temperature, and compared to analogous data for both staggered and eclipsed forms of unbridged ferrocene. The effect of the two-atom bridge, as well as the possibility of a direct metal atom-olefin moiety interaction have been examined in detail. The temperature dependence of the quadrupole splitting is not uniquely related to the tilt angle of the two Cp rings, and is distinct from that observed for related [1]ferrocenophanes. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Since the isolation of the first silicon atom-bridged [1]ferrocenophane by Osborne and Whiteley [1] in 1975, these novel one atom-bridged compounds have been the subject of extensive study, not only because of their use as surface derivatizing agents [2], but more recently as efficient precursors to high molecular weight poly-(ferrocenes) via thermal, anionic or transition metal-catalyzed ring opening polymerization (ROP) reactions [3,4]. [2]Ferrocenophanes, which have been known since the 1960s, have generated similar interest. Numerous crystallographic studies [5,6] of both [1]- and [2]ferrocenophanes have clearly indicated both the extent of 'ring tilt', and have provided an accurate measure of the metal–atom bridging atom (X) distances. In particular, the [1]ferrocenophanes have been examined [7–9] by ^{57}Fe Mössbauer spectroscopy in an effort to elucidate the significance and extent of direct interac-

tion between the iron atom and X. Part of the motivation of the latter studies was due to the observation [10–12] that while the quadrupole splitting (QS) in a large number of ferrocene complexes is rather insensitive to ring substitution, and falls into a quite narrow range, the one atom-bridged ferrocenophanes (tilt angles 14–32°) show a consistently smaller value for this parameter than for those compounds in which the ring planes are parallel. Moreover, this generalization is true for complexes in which the rings are staggered at ca. 295 K (ferrocene and ring substituted ferrocenes), as well as for those in which the rings are eclipsed [13] (C_{60} $(FcH)_2$ and C_{70} $(FcH)_2$, inter alia). ^{57}Fe Mössbauer studies (at room temperature (r.t.) only) for three-, four-, and five-carbon bridged ferrocenophanes have been reported by Nagy et al. [14] and for [2]ferrocenophanes [15] and their Hg(II) and Sn(IV) adducts by Sano and co-workers [16], but do not show any systematic variation in the QS parameter with bridge length.

A rationalization for the lowered QS, as noted above, has been offered by Silver and co-workers [9] who concluded that despite the relatively large distances

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between Fe and X, compared to the sum of the van der Waals' radii, a significant backdonation was still possible, and is assumed to account for the experimental QS results pertaining to [1]ferrocenophanes. In this study, Silver and co-workers [9] also discussed a possible correlation between the QS parameter and the tilt angle (defined as the angle of inclination of the two Cp ring planes) of these complexes. These results were extended in a later study [10] to related [1]ferrocenophanes at ca. 80 K. It should be noted, however, that these Mössbauer results were based on data acquired at a single temperature (at or near liquid nitrogen temperature), and thus the temperature dependence of this parameter has so far not been well established for these compounds, in contrast to the large body of data for ferrocene and related complexes [17]. In fact, it has often been noted in the literature [9,11,12] that the quadrupole splitting in these complexes is relatively temperature insensitive. With the availability of strong ^{57}Co Mössbauer sources, as well as fast-response detectors, it has become possible to examine the temperature dependence of this parameter with greater precision, and a good deal of additional information about these organometallics can be extracted from such data.

In order to further elucidate the contribution of ring-tilt and Fe–X bonding to the electronic structure and the description of bonding interactions in these compounds, in the present study the temperature dependence of the QS, as well as the isomer shift (IS) and the recoil-free fraction (related to A, the area under the resonance curve), have been studied in detail over the range $90 \leq T \leq 295$ K for both the CH_2–CH_2 (**1**) and the CH=CH (**2**) bridged [2]ferrocenophanes. The resultant data were compared to those of ferrocene (complex **3**) and related complexes over the same temperature range. A schematic representation of these compounds is shown in Fig. 1.

2. Experimental

2.1. Metal complexes

An absorber of ferrocene **3** was prepared as described previously [11,12]. The CH_2–CH_2 bridged [2]ferrocenophane **1** (moisture sensitive) was obtained as described earlier by Manners and co-workers [3]. A sample of the
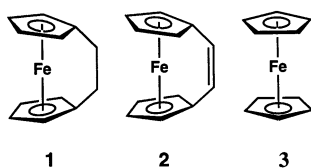

Fig. 1. Schematic representation of the structures discussed in the text.

CH=CH bridged [2]ferrocenophane [ansa (vinylene) Fc] **2** was obtained as described by Buretea and Tilley [4]. Due to their moisture (or oxygen) sensitivity, these compounds were transferred to appropriate sample holders for Mössbauer spectroscopy in a N5 nitrogen (N_2) filled glove box kept anhydrous with P_2O_5.

2.2. ^{57}Fe Mössbauer spectroscopy

^{57}Fe Mössbauer spectroscopy was carried out as described previously [12]. All IS are reported with respect to the centroid of a r.t. spectrum of an 18 mg cm^{-2} metallic iron absorber, which was also used for spectrometer calibration. For T in the range of 90–200 K, in excess of 10^6 counts per channel (of 256) were recorded in each spectrum. At higher temperatures, where the f-factor became very small, up to 8×10^6 counts were recorded to reduce the statistical errors inherent in the data. Experimental errors of the reported parameters were calculated using standard propagation of error techniques and reflect a $\pm 1\sigma$ confidence level. In order to maximize random crystallite orientations with respect to the optical axis of the gamma ray experiment, the microcrystalline powders were mixed with roughly equal weight amounts of BN prior to packing in the sample holders.

3. Results and discussion

The three parameters which can be most readily extracted from ^{57}Fe Mössbauer spectra of these compounds are the IS, the QS and the area under the resonance curve (A), as well as their temperature dependencies. The IS parameter is sensitive to the electron density at the metal nucleus—specifically the density arising from the s-orbitals of the covalent environment. Since the nuclear radius of the excited state of ^{57}Fe is smaller than that of the ground state, an increase in the s-electron density leads to a decrease in the IS, and this effect can be used to distinguish between different electron configurations of the iron atom in various compounds. The temperature dependence of the IS (primarily the second-order Doppler shift) can be related to the effective vibrating mass (M_{eff}) of the metal center.

The QS reflects the symmetry of the charge distribution around the iron atom, and is expected to be non-zero for point group symmetries other than T_d and O_h. The temperature dependence of the QS in most iron-organometallics arises in part from the normal thermal expansion of covalent solids, and is usually small in comparison to the experimental uncertainties involved. The situation in the case of the [1]ferrocenophanes is, however, quite different, and will be discussed below.
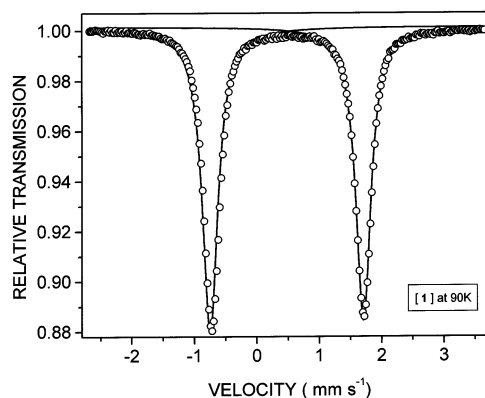
Fig. 2. Mössbauer spectrum at 90 K of **1**. The velocity scale is relative to the centroid of a metallic iron spectrum at 295 K. The full lines are the computer fits to the data, assuming (a) two independent resonance maxima, and (b) Lorentzian (non-saturated) line shapes. Representative linewidth, uncorrected for saturation effects, are 0.283, 0.247 and 0.243 mm s^{-1} at 90, 280, and 330 K, respectively.
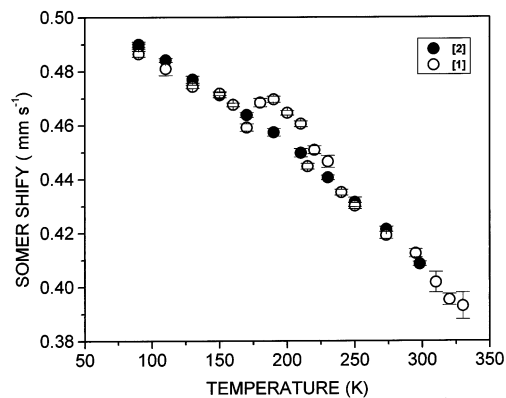

Fig. 3. Isomer shift parameter of **1** (open circles) and **2** (closed circles) as a function of temperature. In this, and the subsequent figures (4–8), the indicated experimental errors are those of the individual data points, and not of a particular regression function.

Finally, it is worth noting that the A parameter is related to the probability of recoilless absorption (and re-emission) of the 14.4 keV gamma radiation in the absorber, and can be related to the mean-square amplitude of vibration of the metal atom in its ligand environment. The temperature dependence of A (specifically ln (A)) can be related [18] to the lattice temperature (Θ_M) of the solid; the smaller d ln (A)/dT the higher Θ_M.

The specific results of such measurements on the subject compounds will now be considered in detail.

3.1. The CH$_2$–CH$_2$ bridged complex **1**

A typical ^{57}Fe Mössbauer spectrum of **1** at 90 K is shown in Fig. 2. (In fact, all of the spectra referred to in this study consist of well separated doublets, which are—at first glance—indistinguishable from each

other.) The IS at 90 K is summarized in Table 1 along with other parameters, and is essentially identical to that of the CH=CH bridged complex (vide infra), but significantly smaller than that of neat ferrocene (staggered rings) and its fullerene intercalates (eclipsed rings). The temperature dependence of this parameter, in contrast to the corresponding data for **2** and **3** (vide infra) shows an unusual behavior for **1**, as is evident from the results summarized in Fig. 3, in which the open circles refer to the CH$_2$CH$_2$ bridged [2]ferrocenophane. From these data it is clear that a significant departure from the usually observed behavior is evident starting at about 160 K, and continuing to about 230 K. Above this temperature, the temperature dependence of the isomer shift again becomes 'normal'.

The quadrupole splitting in the case of ^{57}Fe Mössbauer spectra is given by [17]

$$QS = \{e^2\ qQ/4I\ (2I-1)\}\ [3I_z^2 - I\ (I+1)]\ (1 + \eta^2/3)^{1/2}$$

Table 1
Mössbauer parameters for the compounds discussed in the text

Parameter/compound	1	2	3	C$_{60}$Fc$_2$	C$_{70}$Fc$_2$
IS(90) (mm s^{-1})	0.493 ± 0.003	0.492 ± 0.001	0.531 ± 0.001	0.530 ± 0.003	0.531 ± 0.003
QS(90) (mm s^{-1})	2.427 ± 0.002	2.394 ± 0.001	2.419 ± 0.001	2.390 ± 0.026	2.384 ± 0.006
−dIS/dT × 10^4 (mm s^{-1} K^{-1})	3.62 ± 0.30	3.85 ± 0.10	3.29 ± 0.07[a]	4.22 ± 0.12	2.76[c]
			4.44 ± 0.12[b]		4.88[d]
−dQS/dT × 10^4 (mm s^{-1} K^{-1})	0.98 ± 0.26	1.34 ± 0.07	1.86 ± 0.28[b]		
−d ln (area)/dT × 10^3 (K^{-1})	7.27 ± 0.27	5.32 ± 0.17	∼8.7		
			∼6.0[e]		
Tilt angle α (°)	12.6(4)[f]	23	0	0	0
C$_p$–Fe–C$_p$ angle (°)	164.1(3)[f]		180	180	180

[a] Below λ-point.
[b] Above λ-point.
[c] 86 ≤ T ≤ 170 K.
[d] 170 ≤ T ≤ 375 K.
[e] From Ref. [23].
[f] From Ref. [4].

where I is the spin quantum number, $\eta = (V_{xx} - V_{yy})/V_{zz}$ $(0 \leq \eta \leq 1)$, and V_{ii} are the second derivatives of the potential along the three coordinate axes describing the charge distribution. It should be noted that in the unbridged ferrocenes, to a good approximation, the charge distribution has cylindrical symmetry, so that $V_{xx} = V_{yy}$ and $\eta = 0$. In the bridged ferrocenes, however, the principal field-gradient tensor is no longer normal to the (tilted) ring planes, but now runs through the metal center and the center of the bridging group (X), and has essentially twofold rotational symmetry, although in **1** the C_2 bridge makes an angle of 18.4(1)° with respect to the plane containing the ring centroids and the Fe atom [5]. Moreover, the $Cp_{centroid}$–Fe–$Cp_{centroid}$ angle is 164.1(3)°, compared to its value of 180° in **3** and related unbridged ferrocenes.

It is interesting to note in this context, that the value of QS at 90 K in **1** (2.427 ± 0.002 mm s^{-1}) is, to a first approximation, quite comparable to that of **2** (vide infra) (2.393 ± 0.003 mm s^{-1}) and **3** (2.419 ± 0.001 mm s^{-1}), in contrast to the values reported [7,9,19] for the one-atom bridged ferrocenophanes (2.0–2.1 mm s^{-1}) with comparable tilt angles. The temperature dependence of the QS for **1** is summarized graphically in Fig. 4. In contrast to earlier generalizations, this parameter is indeed temperature-dependent, as may be predicted from the effects of normal thermal expansion on the electric field gradient tensor acting on the ^{57}Fe nucleus. It should be recalled, however, that for covalent solids of the type under discussion, the thermal expansion coefficients are, as a rule, not equivalent with respect to the several crystallographic axes. Hence, it is not possible to predict, only from the molecular symmetry, the sign or magnitude of the temperature dependence of the several components of the field-gradient acting on the iron (probe) atom. In most cases studied to date, the
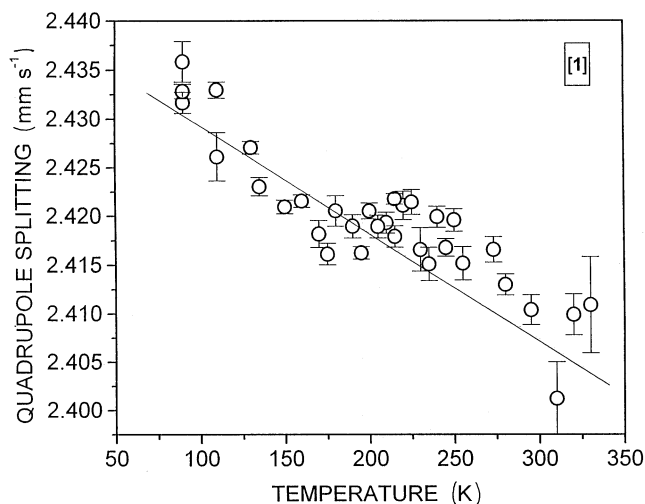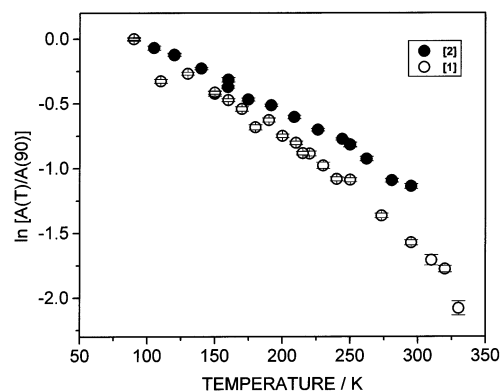
Fig. 5. The ln (area) parameter (normalized to its value at 90 K), for **1** (open circles), and **2** (closed circles) as a function of temperature.

temperature dependence of QS over the range $90 \leq T \leq 330$ K has a (linear) negative slope (the straight line in Fig. 4 is meant as a guide to the eye). Interestingly enough, there is a significant departure from this linearity in the same temperature region as noted above for the IS parameter. These two observations are probably not related to the disorder observed in the single crystal X-ray data reported by Manners and co-workers [5] who noted a 60:40 occupancy ratio in their r.t. data. This disorder, which pertains to the orientation of the C_2 bridges of the molecules within the unit cell, is not reflected in the mean-square-amplitude of the Mössbauer probe atom, as is evident from the temperature dependence of the area under the resonance curve, summarized in Fig. 5, which shows a smooth (continuous) behavior over the above T range. Moreover, the linewidths of the resonances do not show any discontinuity in this temperature range, in consonance with the crystallographic data ($R = 0.0520$) reported by Manners and co-workers [5]. It is more likely that the departure from 'normal' behavior of the IS and QS parameters is related to a phase transition which involves the ring-tilt angle (21.6(4)° at r.t.), but this assumption needs to be tested by a low-temperature single crystal X-ray diffraction study. Such phase transitions, resulting in similar IS(T) and QS(T) behavior have been reported previously [20] in connection with magnon–phonon coupling in rare earth compounds of the type FeR$_2$.

3.2. The CH=CH bridged complex **2**

The relevant temperature dependencies of the Mössbauer parameters for **2** are summarized in Figs. 3, 5 and 6. The numerical and structural data are summarized in Table 1.

A comparison of the isomer shift data for **1** and **2** (Fig. 3) shows that both the high and low T-range values, as well as their temperature dependencies, are (within the resolution limits of the Mössbauer tech-

Fig. 4. Quadrupole splitting parameter of **1** as a function of temperature. The straight line is to guide the eye.
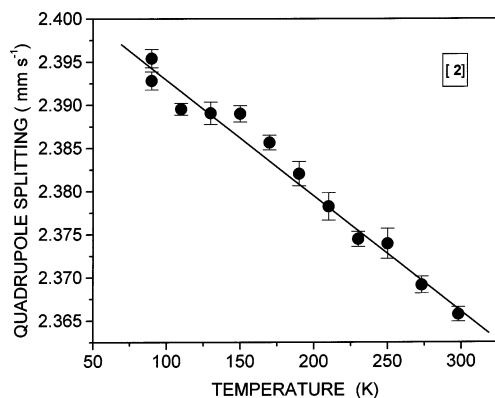
Fig. 6. The quadrupole splitting parameter for **2** as a function of temperature.

nique) indistinguishable. This observation implies that there is no significant backdonation of electrons to the π^* orbitals of the olefinic bridge in **2** (an interaction which is not possible in **1**). Such a backdonation would have manifested itself in a decrease in the IS parameter, since a reduction of the d-electron density would result in reduced shielding of the s-electron density at the nucleus. A comparison of QS(T) for **1** and **2** (Figs. 4 and 6) shows that the QS parameter is significantly smaller in **2** than in **1** (see Table 1), although the temperature dependencies are nearly the same [(-1.34 and $-0.98) \times 10^{-4}$ mm s^{-1} K^{-1}]. Since the QS reflects the shape of the charge distribution around the metal center, the present data can be understood in terms of the electron-withdrawing properties of the olefinic versus the saturated hydrocarbon bridge, invoking only cyclopentadienyl-bridge σ-bonding (rather than direct Fe–X) interactions. Thus, in the case of the two-atom bridged ferrocenophanes, the magnitude of the QS cannot arise solely from the tilt angle of the two Cp rings, compared to unbridged ferrocene.

It is also clear from these data that the smaller QS in the case of the one-atom bridged [1]ferrocenophanes does not primarily arise from the tilt angle of the two Cp rings, but possibly from a bonding interaction between the metal center and the bridging atom. This view has been vigorously advocated by Silver and coworkers [7,9]. In this context it is interesting to note that the Fe–C_B distances (where C_B is the center of the 2-carbon bridge) are ca. 2.66 and ca. 2.76 Å in **1** and **2**, respectively (at r.t.). This is comparable to the reported Fe–Si, Fe–Ge, and Fe–P distances (2.68, 2.74, and 2.77 Å, respectively) in the one-atom bridged ferrocenophanes described by Stoeckli-Evans et al. [21], although they point out that these bond distances, appreciably longer than the sum of the metal-covalent radii (2.37, 2.47 and 2.36 Å, respectively), preclude any significant bonding interaction in these complexes. As noted above, a dissenting view has been articulated by Silver [9], who points out that whereas in the hydrocar-

bon bridged [2]ferrocenophanes there is no energetically available d-orbital to accept electron donation from the Fe atom into the bridging group, in the case of Si, Ge, (and Sn) bridged [1]ferrocenophanes, there are empty 3d orbitals capable of overlap with both e_1 (d_{xy} and d_{yz}) as well as e_2 (d_{xy} and $d_{x^2-y^2}$) iron orbitals. A detailed temperature-dependent Mössbauer study of such one-atom bridged ferrocenophanes is currently underway in these laboratories [19] in an effort to further elucidate the question of this bonding interaction.

3.3. Ferrocene

Finally, it is worth returning to the comparable temperature-dependent Mössbauer data for the parent (unbridged) ferrocene **3** itself. This compound was, in fact, the first organometallic molecule to be subjected to examination by the Mössbauer technique [22], and a large amount of literature exists on this topic [17]. An early, very careful study of both single crystal and microcrystalline ferrocene has been reported by Gibb [23], but reflects, in part, the limitations of the experimentally accessible instrumentation available at the time. In the present study, the temperature-dependent hyperfine parameters of **3** have been re-examined, and extended to somewhat higher temperatures. The crystal structure of ferrocene has been examined at several temperatures, and a detailed heat capacity study has been reported by Edwards et al. [24], who point out that there is no evidence of a sharp change in cell constants at the λ-point (163.9 K). These authors, who also report a subsidiary transition at 169 K, point out that the λ-point transition is a second-order phase transition in agreement with the continuous variation of the lattice parameters. Moreover, the details of the phase transition appear to be strongly dependent on the thermal history of the sample and are, in fact, quite complex. A subsequent more detailed crystallographic study by Seiler and Dunitz [25] showed that at low temperatures the ferrocene molecule is neither staggered (D_{5d}) nor eclipsed (D_{5h}), but is intermediate (D_5) with a rotation angle of 8.7(1)°. In a companion paper, these authors [26] point out that the earlier assumed D_{5d} high temperature form is only *statistically* centrosymmetric and is a superposition of almost eclipsed but purely rotationally disordered structures. A complete review of this problem has been reported by Kubo et al. [27].

As noted by Gibb [23], the IS(T) function for ferrocene is best fitted by a second-order polynomial regression, as shown in Fig. 7, and over the range $90 \leq T \leq 340$ K is of the form IS $= 0.543 - (8.70 \pm 3.63)10^{-5}$ $T - (7.53 \pm 0.96)10^{-7}$ T^2 with a correlation coefficient of 0.995 for 18 data points. There is no appreciable discontinuity observable at the λ-point (163.9 K). In contrast, both the QS interaction (Fig. 8) and ln (area) (Fig. 9) show clearly the hyperfine and
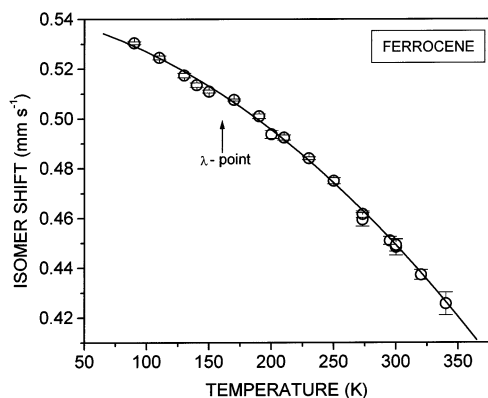
Fig. 7. The isomer shift parameter for **3** as a function of temperature.

Fig. 9. The ln (area) parameter for **3** as a function of temperature.

vibrational consequences of the λ-point transition. The earlier data of Gibb does not suggest a discontinuity at the λ-point of the QS parameter, but such a discontinuity is readily apparent in the ln (spectrum area) versus temperature plot (his Fig. 2). However, his data from the λ-point to 300 K appear to be well fitted by a linear function, while the present data suggest a significant curvature in the regression function over the whole temperature range herein reported. The origin of this difference is not clear at the present time, but may be related (as noted above) to the thermal history and the sequence of measurements of the polycrystalline sample as suggested by Edwards et al. [24]. These data are included in the present study to provide a comparison of the temperature dependence between the hyperfine and lattice-dynamical parameters and the [2]ferrocenophanes and the unbridged ferrocene parent. It is also apparent that the staggered (in ferrocene) and eclipsed (in the $C_{60}Fc_2$ and $C_{70}Fc_2$ intercalation compounds [28], as well as in the [1] and [2]ferrocenophanes) nature of the Cp rings has little bearing on these parameters. This generalization is currently the subject of further study of related organo-tin ferrocenyl complexes in these laboratories [29].
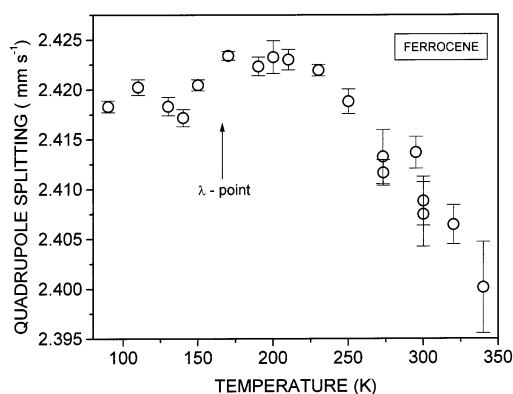
4. Summary and conclusions

The IS and QS parameters, as well as the dynamic behavior of the metal atom in the CH_2–CH_2 and CH=CH bridged [2]ferrocenophanes **1** and **2** have been examined over the temperature range $90 \leq T \leq 300$ K, and compared to the corresponding values for staggered and eclipsed forms of the parent ferrocene itself. The isomer shifts (and their temperature dependence) for both bridged complexes are almost the same, although the detailed behavior in the case of the CH_2–CH_2 bridged complex shows an interesting anomaly (which may be a second-order phase transition) which is not observed in the olefin-bridged homolog. The QS at 90 K in both complexes is very similar to that of the parent ferrocene, but—in contrast to earlier conclusions in the literature—shows a pronounced temperature dependence. In addition, the present data show that the value of the QS parameter is not uniquely related to the tilt angle of the two Cp ring planes, and is different from that observed in [1]ferrocenophanes with comparable tilt angles under similar conditions. The small difference in the QS hyperfine parameter for **1** and **2** is attributed to the slightly greater electron withdrawing effect of the bridge in **2**.

Acknowledgements

Fig. 8. The quadrupole splitting parameter for **3** as a function of temperature.

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